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SURFACE DEFECTS AND THERMODYNAMICS OF CHEMISORBED LAYERS.(U)

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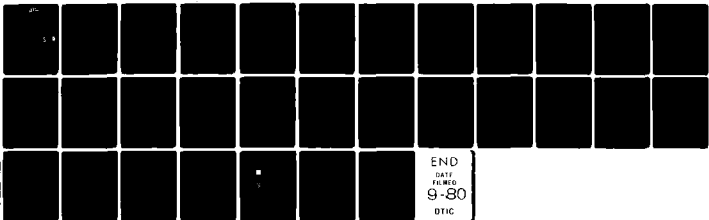
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Abstract

Chemisorbed overlayers on single crystal surfaces can in many cases be considered as lattice gases. The general features of temperature-coverage phase diagrams resulting from attractive or repulsive adatom interactions in such systems are discussed in analogy with binary solid solutions. The effect of surface and overlayer defects on the determination of phase boundaries is considered. The use of low-energy electron diffraction (LEED) to study surface defects and overlayer phase diagrams is briefly summarized.

I. Introduction

Both because of their fundamental theoretical interest and because of their promise in providing a better understanding of adatom interactions, phase transitions in overlayers adsorbed on surfaces have received increasing attention in recent years. Theoretical interest in two-dimensional systems centers around symmetry classification and determination of critical properties.⁽¹⁻⁵⁾ Because there sometimes are no analogues in magnetism or in three-dimensional systems, two-dimensional systems provide the opportunity to study new phenomena. Several experimental methods have been applied⁽⁶⁻¹⁰⁾ in the study of adsorbed layers. The majority of experiments have been done on physisorption systems, with an emphasis on determining the phase diagram and critical exponents.

Studies of chemisorption systems in which phase diagrams have been determined over a range of coverages are much fewer.⁽¹⁰⁻¹⁵⁾ Knowledge of the thermodynamics of such systems may be especially fruitful, however. A force law for the adatom-adatom interaction in chemisorption, because it includes a large substrate-modulated oscillatory contribution, is difficult to establish. Experimental input on the magnitudes of various interactions can aid in its determination. Furthermore, a number of surface phenomena, such as chemisorption, surface chemical kinetics, diffusion, oxidation and passivation, and epitaxy and crystal growth, depend on adatom chemical interactions.

Chemisorption systems frequently can be considered as two-dimensional lattice gases, in that the adsorbate-substrate potential is strong relative to the adsorbate-adsorbate interaction, forcing the adsorbed atoms to sit at discrete sites. In some cases, for example O on W (110), this

adsorbate-substrate binding energy is so strong relative to the diffusional barrier that the vapor pressure of adsorbed atoms above the surface is very small in the temperature range of the phase transitions. If in addition the solubility of adatoms into the bulk (which can be considered in similar terms as adsorption⁽¹⁶⁾) is also small, the adsorption system can be considered to be "closed" (i.e., the chemical potential of the surface phase is different from that of the 3-D vapor phase or the 3-D "gas" dissolved into the bulk, and there is no thermodynamic equilibrium between them), and the surface phase can be considered as one of constant coverage as other thermodynamic variables such as the temperature are changed.

In such situations, it is possible to make some simple analogies with thermodynamics of bulk binary alloys. The purpose of this review is to present these analogies in a more or less pedagogical manner, and to discuss the implications of the existence of substrate surface defects on the interpretation of an overlayer phase diagram in terms of adatom interaction energies.

In the next section, we begin with a discussion of the main simple features of binary alloys that exhibit either complete solubility or phase separation. We relate this to the formation of superlattices of adsorbed atoms ("island" formation). In the third section we consider surface defects and their effect on the phase diagram. In the fourth section we consider very briefly the use of low-energy electron diffraction (LEED) to measure phase transitions in a chemisorbed overlayer, and conclude with a few summarizing remarks.

II. Phase Formation in Binary Systems

A. Bulk Alloys

The "picture" of the thermodynamics of a material is usually a phase diagram, which represents a cut through the n-dimensional space of the chemical potential or partial molar free energy, G , vs. thermodynamic variables, common ones being temperature, pressure, volume, and relative concentration. The phase diagram represents a picture of the most stable phases of all possible ones at given values of the thermodynamic variables, and lines on a phase diagram represent the set of all values of the thermodynamic variables where a component of the system can exist in more than one phase with the same chemical potential. The free energy must always be continuous across a phase boundary. Discontinuities in the derivatives of G with respect to the thermodynamic variables define whether a phase transition is first, second, or higher - order.

Because of its dependence on the enthalpy, G depends on interactions at the microscopic level. If a relation between interaction energies and enthalpy can be established, it is in principle possible to extract interaction energies by fitting the boundaries in a phase diagram.

If one considers a binary system, for example the solution of material A into material B, one can establish some simple relations between the nature of the interaction and features of the phase diagram. We shall consider in particular the temperature-concentration phase diagram.⁽¹⁷⁾ Assuming that the interaction energies in this system are limited to nearest neighbors only, one can write three terms, ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} representing respectively the interaction energies between two A atoms, two B atoms, and an A and a B atom. Then the interaction enthalpy can be written as (quasichemical model⁽¹⁷⁾)

$$\Delta H_m = P_{AB} [\epsilon_{AB} - 1/2 (\epsilon_{AA} + \epsilon_{BB})], \quad (1)$$

where P_{AB} is a pair distribution function, which for a regular solution model⁽¹⁷⁾ is equal to the product of the concentrations of A and B. The heat of mixing, ΔH_m , will be negative when there is a relative net attraction between A and B atoms because $|\epsilon_{AB}| > |1/2 (\epsilon_{AA} + \epsilon_{BB})|$. In this situation A atoms and B atoms will prefer to be close to each other, and upon mixing A and B, a random solution of A and B will result over most of the temperature-concentration range. An ordered AB alloy is possible only over a very limited concentration range, as shown in Fig. 1a. In the opposite case, where A-A and B-B bonds are preferred over A-B bonds, ΔH_m will be positive, and phase separation into α and β phases will occur, Fig. 1b.

An analysis of even these simple phase diagrams yields much information. For a continuous solid solution, A substitutes freely for B from pure B to pure A. In the case of phase separation, at $T = 0^\circ K$ two pure phases A and B exist and there is no mixing. At finite temperatures, since the free energy of mixing ΔG_m depends on the mixing entropy as well as the mixing enthalpy,

$$\Delta G_m = \Delta H_m - T\Delta S_m, \quad (2)$$

and since both T and ΔS_m are always positive for $T > 0^\circ K$, the entropy term tends to make a disordered phase (random solid solution) more stable as the temperature increases. Hence when there is phase separation, phases α and β , consisting respectively of a matrix of A with B dissolved in it and vice versa, become stable over increasing concentration ranges as the temperature is raised, and the two-phase region becomes correspondingly smaller as indicated by the inward motion of the phase boundaries. At some critical temperature and concentration the difference between α and β disappears

and the system becomes a single phase above this temperature.

The amount of each phase and its composition can be directly determined from the phase diagram. For any temperature T and composition X_B in a single-phase region, the amount of the phase is always equal to the total amount of material and its composition is uniform and equal to X_B of B and $(1-X_B)$ of A. For any temperature T' and composition X'_B that fall into a two-phase region, the compositions of the two phases are given by the intersections $X_B^{(s)}(\alpha, T')$ and $X_B^{(s)}(\beta, T')$ of the isotherm at T' with the phase boundaries. The amounts of the phases α and β present at the condition X'_B, T' are given by the lever rule;⁽¹⁷⁾ e.g., the amount of β at X'_B equals $\% \beta = \frac{x}{L} = \frac{X'_B - X_B^{(s)}(\alpha, T')}{X_B^{(s)}(\beta, T') - X_B^{(s)}(\alpha, T')}$. (3)

As can be seen from the discussion of enthalpy and entropy, phase separation must occur at some (low) temperature if A-A or B-B bonds are preferred over A-B bonds. At sufficiently high temperatures the system will always reduce to a single phase (be it only the gas phase). Of course, in actual situations many more complex intermediate phases are possible.

B. Ordering of an Adsorbed Overlayer

We assume adsorption of a gas randomly into lattice sites on a perfect surface of infinite lateral extent. This system can be immediately considered in terms of the binary alloy just discussed if the adatoms are identified with material B, and the vacant lattice sites with material A. We thus can draw a temperature - composition diagram, with the "concentration of B" now replaced by "coverage".

The simple features of phase separation or random solid solution formation carry through directly. If both the barriers to evaporation and solution of the adsorbate into the bulk are large relative to the

barriers for diffusion, then at sufficiently high temperatures (corresponding to the dominance of the mixing entropy term over the enthalpy of mixing noted earlier) the adsorbate will exist as a single phase, a random lattice gas. Although the adatoms are still preferentially bound in lattice sites the probability of hopping from one site to another in the surface is large.

If no lateral interactions are present, corresponding to zero enthalpy of mixing, a random solution will persist at all temperatures. At low coverages this will be a random solution of adatoms in the empty lattice sites ("lattice vapor") while at high coverages it will be a random solution of vacancies (empty lattice sites) in an ordered $p(1 \times 1)$ structure that is produced by the increase in "pressure" arising from the high coverage.

Interactions, however, invariably exist, and these can be either net attractive or net repulsive.⁽¹⁸⁾ Consider as the first case a lattice gas with nearest-neighbor attraction and all other interactions equal to zero. Since there is a net attraction, the adatoms will form an ordered $p(1 \times 1)$ phase. In terms of the discussion on binary alloys, if $\epsilon_{BB} = \epsilon_{ad-ad}$, $\epsilon_{AA} = \epsilon_{vac-vac}$, and $\epsilon_{AB} = \epsilon_{vac-ad}$ are respectively the adatom-adatom, the vacancy-vacancy, and the adatom-vacancy interaction potentials, then in simplest terms $|1/2 (\epsilon_{AA} + \epsilon_{BB})| > |\epsilon_{AB}|$ and phase separation will occur, at least at $T = 0^\circ K$, and Fig. 1b is directly applicable. This is the well-known phenomenon of "island formation" in overlayers, although this is a misnomer, since the equilibrium state will consist of only one ordered $p(1 \times 1)$ phase and one nearly empty "sea". The phase boundaries represent the locus of T and θ for the coexistence of the $p(1 \times 1)$ and the disordered phase, the relative amounts of these at any coverage being given again by the lever rule. As before, with increasing temperature the single-phase regions grow at the expense of the two-phase region because of the entropy term, with these

single-phase regions containing more and more "solute" of the opposite species. On the low-coverage side the coverage at the phase boundary for any T can be considered as the two-dimensional vapor pressure of the ordered $p(1 \times 1)$ region at that T , or equivalently, the saturation solubility of adatoms in the "sea" at that T . By analogy, the high-coverage phase boundary represents the saturation solubility of vacancies in the ordered $p(1 \times 1)$ phase.

In a classic paper, Lee and Yang⁽¹⁹⁾ provided an analytical solution for two-dimensional binary systems by transforming the magnetic Ising model to the lattice gas model, using a nearest-neighbor attractive interaction, ϵ . For an adsorbed layer ϵ is identified with ϵ_{ad-ad} , the attractive interaction energy that leads to formation of an ordered structure, and the relation between coverage and the interaction energy is⁽²⁰⁾

$$[2\theta(>1/2, T) + 1] = -[2\theta(<1/2, T) + 1] = [1 - 1/\sinh^4(\epsilon/2 kT)]^{1/8}, \quad (4)$$

which gives a critical coverage $\theta_c = 1/2 \theta_{saturation}$, and a critical temperature T_c directly related to the attractive interaction by the well-known Onsager solution.⁽²¹⁾ Their results are shown schematically in Fig. 2. The phase transitions are first-order except at θ_c , where it is second-order.

Although $p(1 \times 1)$ phases are interesting in their own right, e.g. in crystal growth, chemisorbed-overlayer superlattices with larger unit meshes are frequently observed. The above analysis can be easily extended (at least in an approximate way)⁽²⁰⁾ to non- $p(1 \times 1)$ overlayers by redefining the lattice ("prefacing" transformation⁽²²⁾) so that there are again no unoccupied sites for a (saturation-coverage, $0K$) superlattice. This is illustrated in Fig. 3. For example, a $c(2 \times 2)$ structure indexed relative to a square substrate lattice will form a $p(1 \times 1)$ structure indexed relative to a lattice of bridge-bonded sites. Similarly, for a $p(2 \times 2)$ layer, a $p(1 \times 1)$

structure can be obtained with a prefacing transformation using four-fold sites.

The Lee-Yang model⁽¹⁹⁾ then applies directly to any superlattice that can be transformed to a $p(1 \times 1)$ structure. The model will give a critical point at $\theta_c = 1/2 \theta_{sat}$ for that superlattice structure. In the absence of symmetry breaking⁽²⁰⁾ (discussed below), the phase boundaries will be symmetric around θ_c . If a single attractive interaction is assumed, it can be solved for exactly by fitting Eq. (4) to the phase boundaries.⁽²⁰⁾

In summary, if a net attractive interaction exists between adatoms, phase separation will occur below some temperature for coverages below saturation coverage. This temperature is a rough measure of the net attractive interaction. Additionally, the existence of a phase at a coverage below that at which it can exist as a single phase containing vacancies implies phase separation and hence a net attractive interaction.

Repulsive interactions between adatoms are the analogue of preferential A-B bonding in alloys, in that an adatom prefers to have vacancies next to it rather than other adatoms. As a result, the adsorbed layer attempts to form a single phase (a "solution" of adatoms and vacancies) for as large a range of coverage as the repulsion is able to support. For non- $p(1 \times 1)$ superlattices repulsive interactions are, of course, present between near-neighbors and also perhaps for larger distances, but the net interaction is attractive. In some cases the interaction may appear completely repulsive, although it seems in general reasonable that there be at least a weak attraction, so that at sufficiently low temperatures a two-phase region will again form.

Binder and Landau⁽²³⁾ have considered a square lattice with a nearest-neighbor repulsion, J_{n-n} and a next-nearest neighbor interaction J_{n-n-n} that can be attractive, repulsive, or zero. Figure 4 shows their results for J_{n-n-n}

attractive and zero. For J_{n-n-n} attractive they find, as before, a two-phase region centered about $\theta_c = 1/2 \theta_{sat}$, where for this structure $\theta_{sat} = 1/2$. This two-phase region shrinks to zero when J_{n-n-n} goes to zero, and only a single phase is stable. It should be noted that in the former case, a $c(2 \times 2)$ structure [covering part of the surface] will appear already at very low coverage [giving rise to a LEED pattern], whereas in the latter case, a $c(2 \times 2)$ structure does not appear until $\theta \approx .35$; this point is analogous to a percolation threshold.⁽¹⁾ When the $c(2 \times 2)$ phase does form for the repulsive case, it covers the whole surface, but contains a sufficient number of vacancies to give the proper coverage. Below $\theta \approx .35$, although there may be fluctuations with short-range order, no long-range order is possible.

The maximum temperature at which the one-phase region is stable is determined by the strength of the repulsive interaction. If this were infinite, [e.g. in a $p(1 \times 1)$ layer constrained to remain on lattice sites] this temperature would also be infinite. (Actually other processes take place, such as desorption or occupation of sites out of the two-dimensional layer). For finite repulsions, the transition at θ_{sat} for a given non- $p(1 \times 1)$ layer represents a true order-disorder transition into the unoccupied repulsive sites, with a transition temperature determined by the potential energy difference between the attractive and repulsive sites. At lower than saturation coverage, it is easier for the system to transform, because of the vacancies that already exist in the ordered structure.

The transformation at θ_{sat} is second-order, and the transformations below θ_{sat} out of the one-phase region to the lattice vapor phase are most likely also second-order, as shown in Fig. 4. The point where the phase boundaries meet is a tri- or multicritical point.

Before leaving this simple treatment of the main features of an adsorbed-layer phase diagram, several things should be noted. One, the phase diagram

in Fig. 4 is shown symmetric about θ_{sat} . This is never the case. As more atoms are forced into the lattice than are required for saturation, because of three-body repulsions the ordered structure quickly becomes less stable and the system begins to separate into a higher-density ordered (or disordered) phase and the initial saturated phase. This simply says that the equilibrium concentration of "interstitials" in a phase at a given T is less than that of vacancies, analogous again to bulk alloys. The strength of three-body interactions can in some cases be determined from the asymmetry of the phase diagram.⁽²⁴⁾

Second, it is of course possible to have saturation coverages at other than $\theta = 1/2$ [e.g. $\theta = 1/3$ for $(\sqrt{3} \times \sqrt{3})$ in fcc (111)], and it is as a result possible to have exceedingly complex phase diagrams as one passes from one ordered phase to another. This is demonstrated succinctly by the model calculations of Berker and Ostlund,⁽²⁵⁾ who consider adsorption on a hexagonal face and vary the strength of different interactions, keeping the nearest-neighbor interaction infinitely repulsive. They are able to produce a variety of phase diagrams and two ordered phases; as a result of their infinite nearest-neighbor repulsion, the $(\sqrt{3} \times \sqrt{3})$ structure is the densest one allowed, but a $p(2 \times 2)$ phase is produced at lower coverages.

Experimentally, several phase diagrams for lattice gas systems have been determined in recent years, at least over part of the total range of coverages. These include S/Cu(110),^(10a) S/Au(110),^(10b) S/Pt(111),^(10c) O/W(110),⁽¹²⁾ H/Mo(100),^(15a) H/W(100),^(15b) O/Ni(111),⁽¹⁴⁾ and H/Ni(111).⁽¹³⁾ All of these except the last show two-phase regions indicating net attractive interactions. It is not known whether H/Ni(111) represents a true case of repulsive or zero interactions at all distances, or whether at a lower temperature a two-phase region exists.

III. Surface Defects

In discussing the thermodynamics of adsorbed layers it is generally assumed that both the substrate and the overlayer are free of defects that limit the long-range order in the overlayer. This is, of course, almost never the case, and anything that affects long-range order of the overlayer may affect the stability of phases. This is principally because of edge or boundary energy in the adsorbed layer or the potential associated with a substrate defect. The nature of a substrate defect (i.e., does it raise or lower the free energy of the overlayer?) is also important. Single-phase and two-phase regions may be affected in different ways. Since one of the aims of determining phase diagrams in chemisorbed systems is extracting interaction energies, it is important to recognize how the phase boundaries may be affected by the existence of defects.

We consider three types of extended defects, mosaic structure in the substrate, steps on the substrate, and antiphase domains in the overlayer. More complex situations can exist, of course, such as antiphase domains in reconstructed substrates or any combination of the above defects, but these three serve to illustrate the difficulties inherent in interpreting phase diagrams assuming long range order.

A mosaic structure is a small orientational or translational misalignment of crystalline regions of finite size. No phase correlations exist between different crystallites: the surface acts like a collection of independent small surfaces. (In a diffraction experiment, one would observe a physical or "particle-size" broadening of the reflections).

A step on a surface, on the other hand, represents a defect in which the phase correlation between one region (a "terrace") and another is preserved. In a diffraction experiment, this manifests itself in an alternate broadening (or splitting) and narrowing of reflections.⁽²⁶⁾

For both types of defects, a diffusional barrier is likely to exist at the edge of the ordered region, as shown in Fig. 5. The existence of such a barrier can be explained⁽²⁷⁾ in terms of a reduced coordination for an adsorbate atom as it reaches the edge, and thus a reflection toward the interior of the terrace. Because of the increased coordination at the lower edge of the step, there is a local potential minimum that acts as a nucleation site. Such a local minimum may also exist at the top of the step (and hence also for the mosaic crystallite surfaces), as indicated by field ion microscopy measurements of adatom diffusion.⁽²⁷⁾

In any case, if the diffusional barriers at the edge are high relative to the diffusional barriers away from the edge, adatoms initially adsorbed on a terrace or mosaic surface are constrained to remain there, and for all intents each terrace or mosaic surface forms its own small thermodynamic system or "pot".⁽²⁸⁾ (If the diffusional barrier is higher than the desorption or solution barrier, the isolation is, of course, absolute).

For such finite systems, island boundary energies, defect potentials, and limited correlation lengths become important. Considering first the two-phase region, if one makes the simplest assumption of random adsorption and neglects any potential energy contribution due to adsorption at a substrate defect, then each "pot" will contain one ordered region of limited size and one vapor region of limited size. As opposed to a macroscopic ordered phase, in each of these islands (as they now really are) the boundary-to-area ratio becomes large, and the boundary energy can be a significant fraction of the total free energy. Because it is positive it makes the ordered region less stable, i.e., the vapor phase will grow at the expense of the island. A quantitative measure of the magnitude of this effect can be obtained from the Thomson-Freundlich equation,⁽¹⁷⁾ which relates the solubility of

small particles to their size, surface tension, and mass. Assuming this equation can be used directly for two dimensional phases by relating the boundary-to-area ratio of an island to the surface-to-volume ratio of a particle, a typical adsorbed gas may have a roughly 20-30% greater solubility than a macroscopic ordered region, i.e., the low-coverage phase boundary moves to the right, increasing the stability region of the vapor phase.⁽²⁹⁾ In fact, the lower the coverage (and hence the smaller the islands), the greater the deviation, as the boundary energy takes on increasing importance.

Are regions as small as this realistic on surfaces? Certainly they are as far as steps are concerned. A surface oriented to within $1/2^\circ$ of a given direction will have a step roughly every 40 to 50 atoms. Sputtering and annealing generally increase the surface damage. A mosaic structure with domains as small as this is not likely for crystals grown from a melt or for recrystallized samples, but epitaxially grown films may contain very small domain sizes. Recently an average domain size of $\sim 75\text{\AA}$ was measured on a Ag(111) film epitaxially grown on mica.⁽³⁰⁾

Indications of the boundary energy dependence of the adsorbed island size as a function of coverage were seen for O on W (110).^(28, 31)

A more complicated model would take into account the potential energy of adsorption of a substrate defect. For a step, the most favorable sites would be at the lower edge. Nucleation sites, of course, lower the total energy and thus make the ordered region more stable. Since potentials associated with defects are likely to be short-range, they should be important only for a very small islands. One can imagine, however, pathological cases in which a strong defect-associated potential along two edges of a step forces an island to grow with a concave boundary, making the island more stable than an infinite one.

The implications in a one-phase region are less simple. If one has a finite-size region, there will be only limited correlation lengths. Without a defect potential there may not be any effect on the phase boundary. Assuming a nucleation potential at one edge of a finite region but not on the other, Berker and Ostlund⁽³²⁾ have shown that near the temperatures and coverages in the phase diagram where the second-order boundary meets the first-order boundary, the system attempts to phase separate (because of the existence of the ordered phase at the edge with the defects but not the other) at temperatures and coverages where an infinite system would already have formed a single phase. Thus, the two-phase region broadens and moves up in temperature, and there is no sharp multicritical point.

Finally, in overlayers with a non- $p(1 \times 1)$ superlattice, translation or rotational antiphase domains are possible and in fact likely. Phase correlations are obviously preserved in going from one domain to another. In a diffraction experiment, the spot broadens because of this antiphase interference effect.

Because it is very difficult to remove domain boundaries, even for a perfect substrate, one must consider that the domain boundary energy is included in any measurement of the thermodynamic properties of the overlayer. For a substrate with defects, there is, of course, no hope of removing different translational or rotational domains, although it is possible to nucleate only one rotational domain by careful preparation of the surface.⁽³³⁾ However, since each "pot" on the surface is expected to contain only one domain, and the pots are assumed not to interact thermodynamically, antiphase domains are not important for substrate surfaces with a reasonable step density or small mosaic size.

Because of the domain boundary energy, the effect of antiphase domains on a two-phase region is the same as for finite island size, i.e., an increase in the solubility of the ordered adatom regions in the vacancy "sea" at a given temperature, and thus a decrease in the extent of the two-phase

region. In a one-phase region, the effect is less clear, but will probably also be the same as that of a finite size.

IV. Measurement of Phase Diagrams and Surface Defects

Space does not permit a detailed treatment of methods to measure the properties discussed in this review. It is clear, however, that diffraction techniques lead the way, because of the possibility of directly observing the pair correlation function. The technique most commonly used for observation of ordered chemisorbed phases and transitions in these is LEED. By measuring the decay of the peak intensity of superlattice reflections with temperature as well as the angular distribution of intensity in a superlattice reflection with temperature, the phase diagram of the overlayer can be established.⁽¹⁰⁻¹⁵⁾ Defects on surfaces can also be readily studied by LEED. Major emphasis has been placed on steps,⁽²⁶⁾ but recently it has also been possible to determine mosaic structure⁽³⁰⁾ in surfaces and to approach a quantitative description of antiphase domains.⁽³⁴⁾

However, there remains a large number of difficulties, especially in the interpretation of the peak intensity measured in LEED, and its relation to the properties that one wishes to observe. For example, the interpretation of the intensity decay is different for a transition out of a two-phase region into the vapor phase than it is out of a one-phase region. The simplest conceptually is the transition at saturation coverage for a given overlayer structure. Here the transition is a true order-disorder transition, with adatoms moving from the "correct" sites to substitutional "wrong" sites. A measurement of the decay of the superlattice beam peak intensity is a measure of the order parameter, and in the ideal situation (i.e., for an ideal instrument and a perfectly ordered overlayer and defect-free substrate) it should be possible to obtain the transition temperature from the extrapolation of the inflection point to zero intensity, as well as correct critical exponents, and to classify the nature of the transition.^(2, 3) In practice, this is confounded by instrumental effects, in particular the detector width, which typically allows a large degree

of diffuse scattering to enter any measurement of the peak intensity.⁽³⁵⁾

In a limit of a detector the size of the two-dimensional Brillouin zone, no intensity decay is observed as one goes through a phase transition. Additionally substrate defects and antiphase domains can profoundly affect the intensity decay even for a perfect instrument. Thus, if either antiphase domain boundaries exist or if steps exist and the data are not taken at the minimum in the angular widths as a function of energy,⁽²⁶⁾ the peak intensity will decay more slowly than it would for a perfect layer.

These problems can be surmounted by measuring the relevant parameters, of course. Thus the critical scattering can be measured or estimated, and steps and domain boundaries can be estimated. It is, of course, possible to extract "critical exponents" from any intensity decay, but without such considerations the results are probably not reliable. Recent attempts to extract critical exponents apparently have met with this difficulty.⁽³⁵⁻³⁷⁾

Away from saturation coverage, the measurement of the peak intensity has a different meaning. In a two-phase region, the peak intensity comes only from the ordered regions (except for a gas-scattering background that is small at low temperature). A measurement of the intensity J , versus temperature then simply measures the disappearance or dissolution of the ordered phase. The shape of the J vs. T curve is determined by the shape of the phase boundary. For a temperature range where this phase boundary is nearly vertical, the intensity will not drop with temperature (other than due to the Debye-Waller factor), because the solubility remains constant. Conversely, when the phase boundary becomes nearly flat, the intensity will decay very rapidly with temperature. If a phase boundary had a constant slope, the intensity would decay as the square of this slope. If one takes the Lee-Yang model as an example of a two-phase boundary, it is easy to see why the temperature decay J vs. T frequently look similar to what is observed at saturation coverage. However, the major difference is that the phase boundary should be put at the temperature

where the intensity goes to zero rather than at an inflection point. This is very difficult to measure because at this temperature all atoms are in the disordered phase, and this "vapor" gives a gas scattering background and can be quite large.

The angular width of diffracted beams also gives information about the ordering on a surface, and may help to distinguish different situations. In a one-phase region, the ordered phase should always be as large as that allowed by substrate heterogeneities. Thus, if the substrate domains or terraces are small, the spots should be broad, but there should be no coverage dependence to the angular width of diffraction spots, and with increasing temperature they should show a very sudden broadening at the phase boundary, due to the existence of only short-range order above the transition temperature.

In a two-phase region, the angular widths should reflect the size of the ordered region. If the substrate is perfect, there should be no dependence of angular width on coverage except at very low coverages. This is because, if equilibrium is assumed, there will be only one large ordered phase, which even for fractional percent coverages is larger than the resolving power of the LEED instrument.⁽³⁴⁾ It is not likely that the diffracted intensity is sufficient to observe such low coverages. If the substrate contains defects, and the adatoms are assumed to be randomly distributed in the "pots", a beam broadening will be observed at low coverages as many small islands form. There should be a narrowing of beams with increasing coverage at fixed temperature, as islands in each "pot" grow. This has been observed.⁽²⁸⁾ There should also be a temperature dependence. Increasing the temperature at a fixed coverage should lead to beam broadening, as islands within each "pot" evaporate into the "sea". This has also been observed.⁽¹²⁾

Beam broadening can be used to distinguish between different models of filling terraces or domains. If instead of random filling, some pots are completely filled (because they have perhaps favorable defect sites) while others remain essentially empty, the coverage dependence of the beam broadening vanishes, the broadening being given at all coverages very nearly by the finite-size effect of the substrate.

All of this assumes true equilibrium. There may be quite long-lived metastable states that complicate this simple picture. Thus islands may form even on perfect surfaces if there are a large number of defect sites for adsorption and diffusion rates are slow.

Finally, there are more complex situations, such as transitions from a two-phase region to a one-phase region with the same ordered structure, transitions from a one-phase region to a vapor at less than saturation coverage, and transitions from a mixture of two ordered phases to a disordered one. There are so far no measurements of these types, although it should be possible from a careful analysis of the LEED intensity profiles and their temperature dependence to determine accurate phase boundaries for these cases also.

We have not considered cases of registered-to-incommensurate transitions, which can be studied using LEED,⁽³⁸⁾ but which can't be described with the simple analogies discussed here.

V. Conclusions

We have discussed in this review the main features of simple phase diagrams in overlayers that can be considered lattice gas systems. By analogy with the thermodynamics of bulk binary alloys, we have illustrated the relation of the overlayer structure and the coverage if simple net attractive or repulsive interactions are assumed. Actual overlayer systems may, of course, have more complex interactions, but if these lead to additional features in the phase diagram, it should be possible to extract the interactions by fitting the phase boundaries.

A major concern in determining adatom interactions by fitting the phase boundaries is defects in the substrate or the overlayer that limit the long range order in the latter or provide nucleation sites. As a result, additional terms enter into the interaction enthalpy. The most important defects are probably antiphase domain boundaries, and their effect is least well understood. Substrate steps also will be important in such cases where the diffusional barrier at the edge of the step is sufficiently large to provide effective isolation between atoms adsorbed on different terraces. Steps may also provide strong defect sites for preferred adsorption. Mosaic structure is probably less /important unless the mosaic size becomes very small. This has been observed in epitaxially grown thin films⁽²⁹⁾ and may also result when crystal surfaces cut and polished or cleaved from a bulk crystal are frequently sputtered and reannealed.⁽³⁹⁾

Phase diagrams as a function of coverage and temperature are in many cases most readily measured by LEED. Defect structures of surfaces and overlayers can also be determined with this method. Research is just beginning in these areas, but it appears to be a quite fruitful approach for determining interactions between adsorbate atoms in a variety of applications.

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FIGURE CAPTIONS

Figure 1: Simple phase diagrams for binary alloys, AB.

- a) Case of preferred A-B bonding, leading to a random solid solution, α , over most of the temperature-coverage range. A region of ordered phase, α' , shown at low temperatures, can exist over only a limited concentration range. Transitions are assumed second-order between α' and α .
- b) Case of preferred A-A and B-B bonding, leading to phase separation. At $T=0K$, pure A and pure B coexist. At any finite temperature T' , α and β coexist with compositions given by the intersection of the isotherm T' with the phase boundary. Transitions from the two-phase to the one-phase region are first-order. The dashed lines indicate the application of the lever rule to the determination of the amounts of phases α and β present at any average composition X'_B at T' .

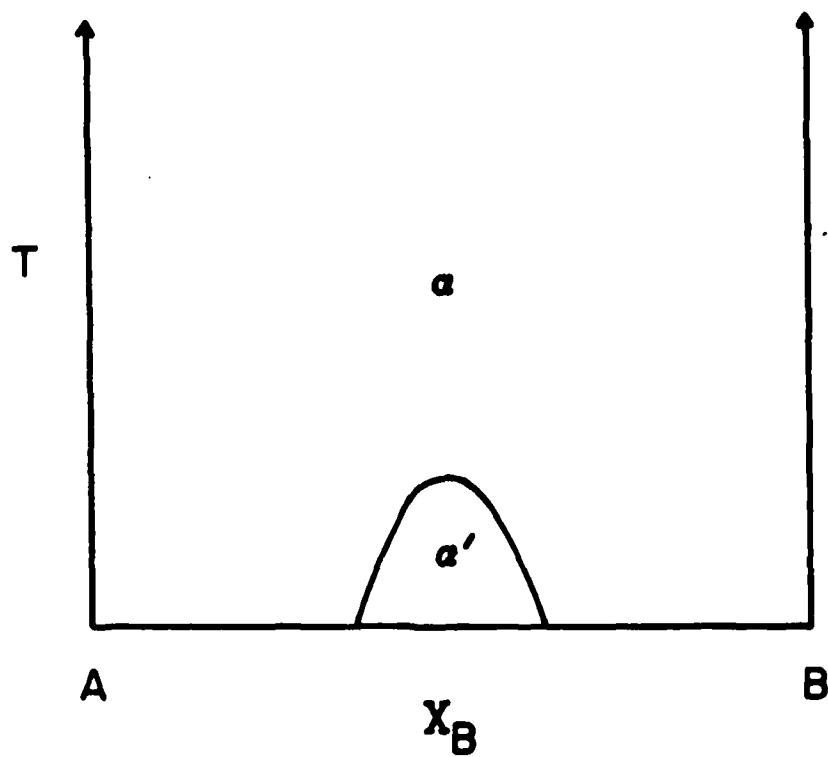
Figure 2: Schematic diagram of the solution of the Lee-Yang model for a lattice gas with a net attractive interaction, giving the phase boundary separating the two-phase from the one-phase regions. Phase 1 is a lattice vapor; phase 2 is a $p(1 \times 1)$ ordered structure. At $T=0K$ a dense $p(1 \times 1)$ solid (x) coexists with an empty "sea" (○). At finite temperatures, the $p(1 \times 1)$ phase contains vacancies and the "sea" contains atoms. Above the critical temperature, T_c , only one phase exists.

Figure 3: Schematic illustration of the use of the lattice-gas model with net attractive interactions but near-neighbor repulsions, leading to non- $p(1 \times 1)$ structures, a) $p(1 \times 1)$ structure, b) $c(2 \times 2)$ structure. In b) the new lattice has unit vectors $\sqrt{2}$ times the substrate unit mesh and rotated by 45° . The critical coverage referred to this overlayer lattice remains equal to 0.5, but referred to the substrate lattice it becomes $\theta = .25$. Thus a two-phase region should appear centered about $\theta = 0.25$.

Figure 4: Phase diagram for a $c(2 \times 2)$ overlayer structure with nearest-neighbor repulsion and next-nearest-neighbor interaction attractive (upper panel) or zero (lower panel), from Monte Carlo calculations. The upper panel shows the situation typical for chemisorbed layers with superlattices. The saturation coverage for the $c(2 \times 2)$ phase is $\theta = 0.5$. Real phase diagrams are never symmetric about the saturation coverage. (After Binder and Landau, Ref. 23).

Figure 5: Schematic diagram of the potential energy of the surface layer for a terrace and for a finite-size crystallite. There is a diffusional barrier at both up and down steps of a terrace, as well as a potential energy minimum associated with the lower edge of a step. A potential energy minimum is also possible at the top of a step. For a finite-size crystallite, the potential barrier may equal the desorption barrier (solid line), or it may be lower (dashed line) if the discontinuity between two crystallite surfaces of a mosaic is small.

a)



b)

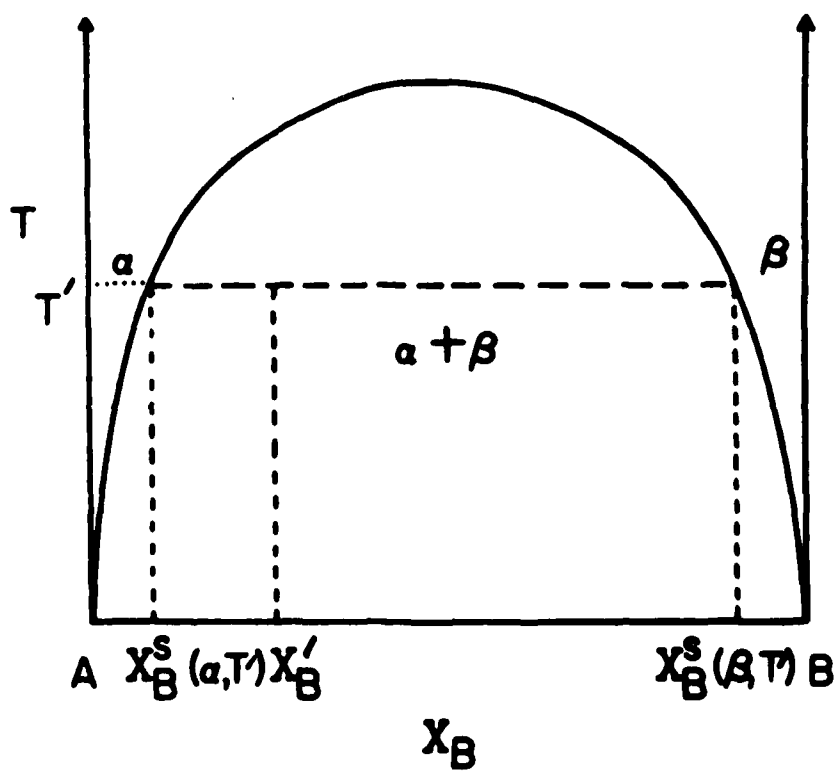


Fig. 1

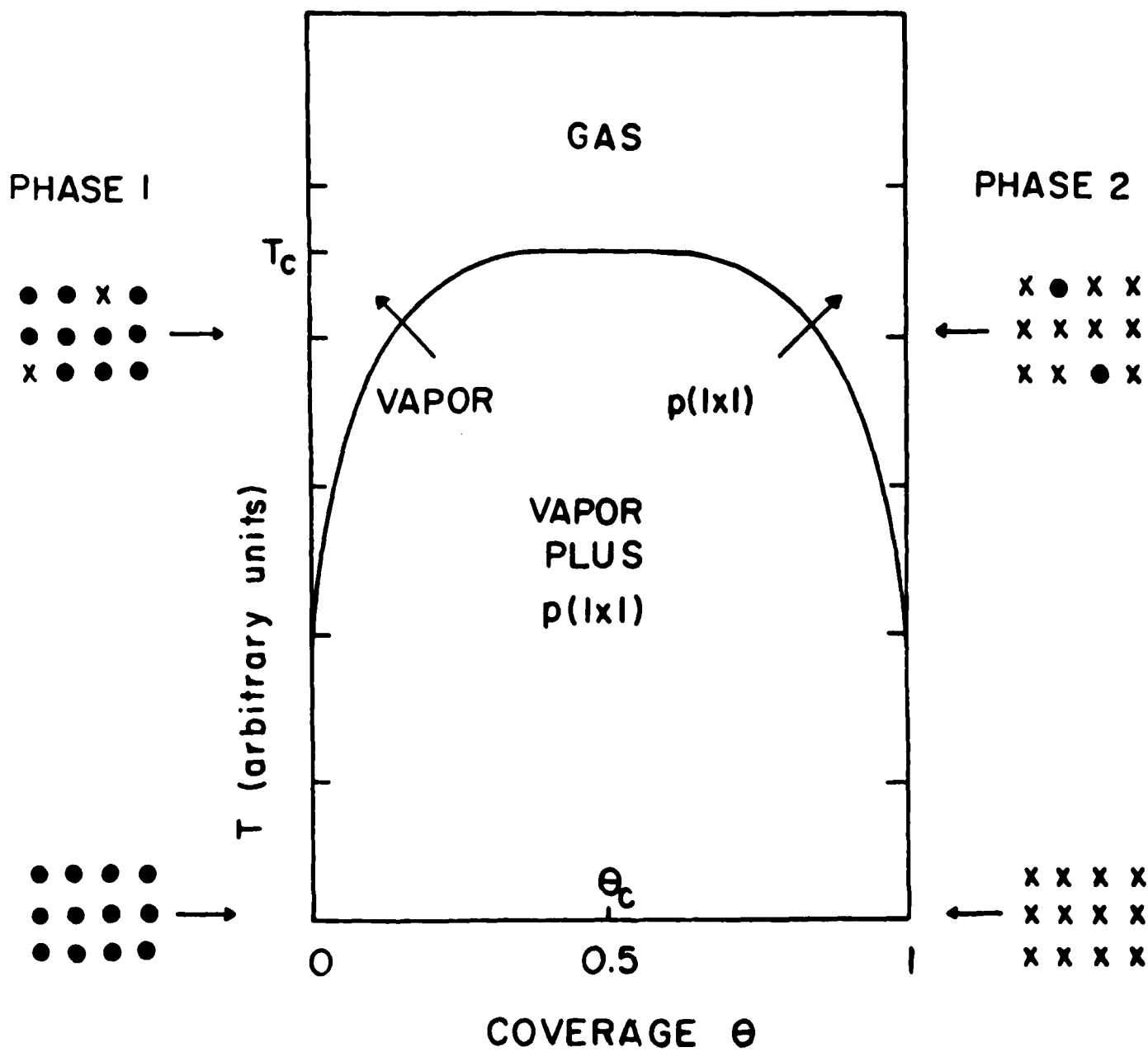


Fig. 2

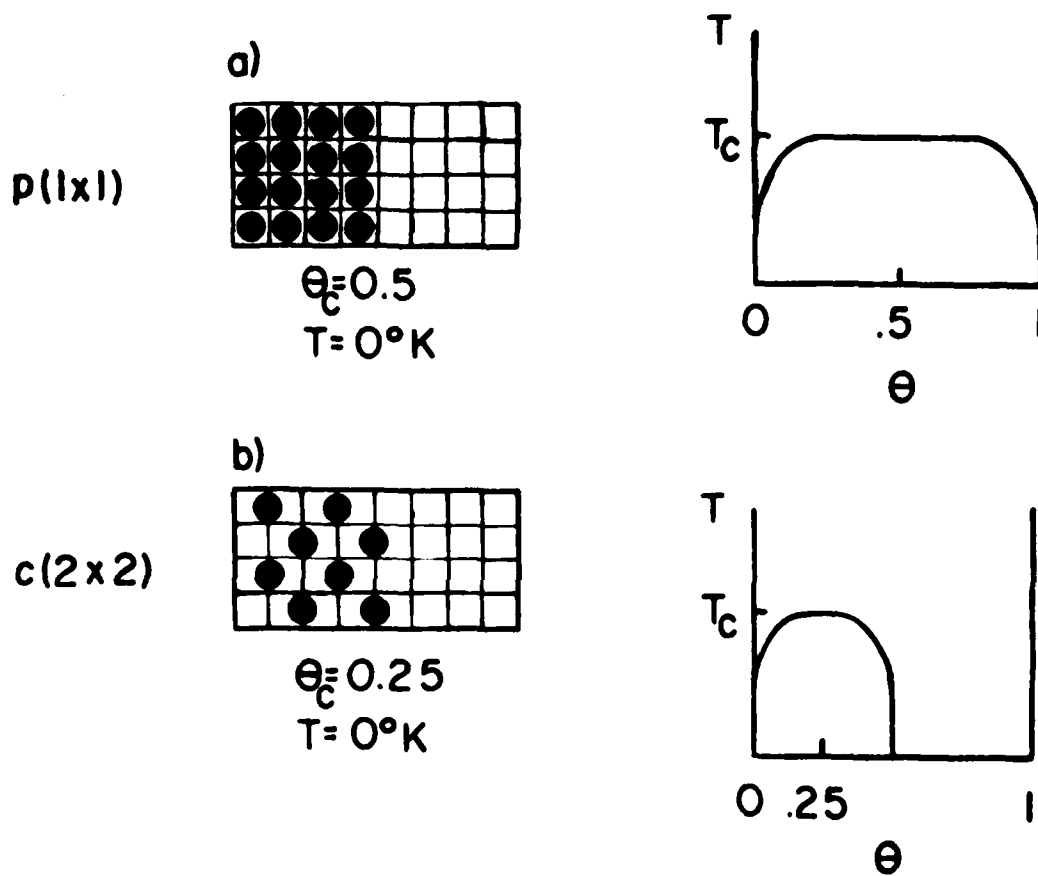


Fig. 3

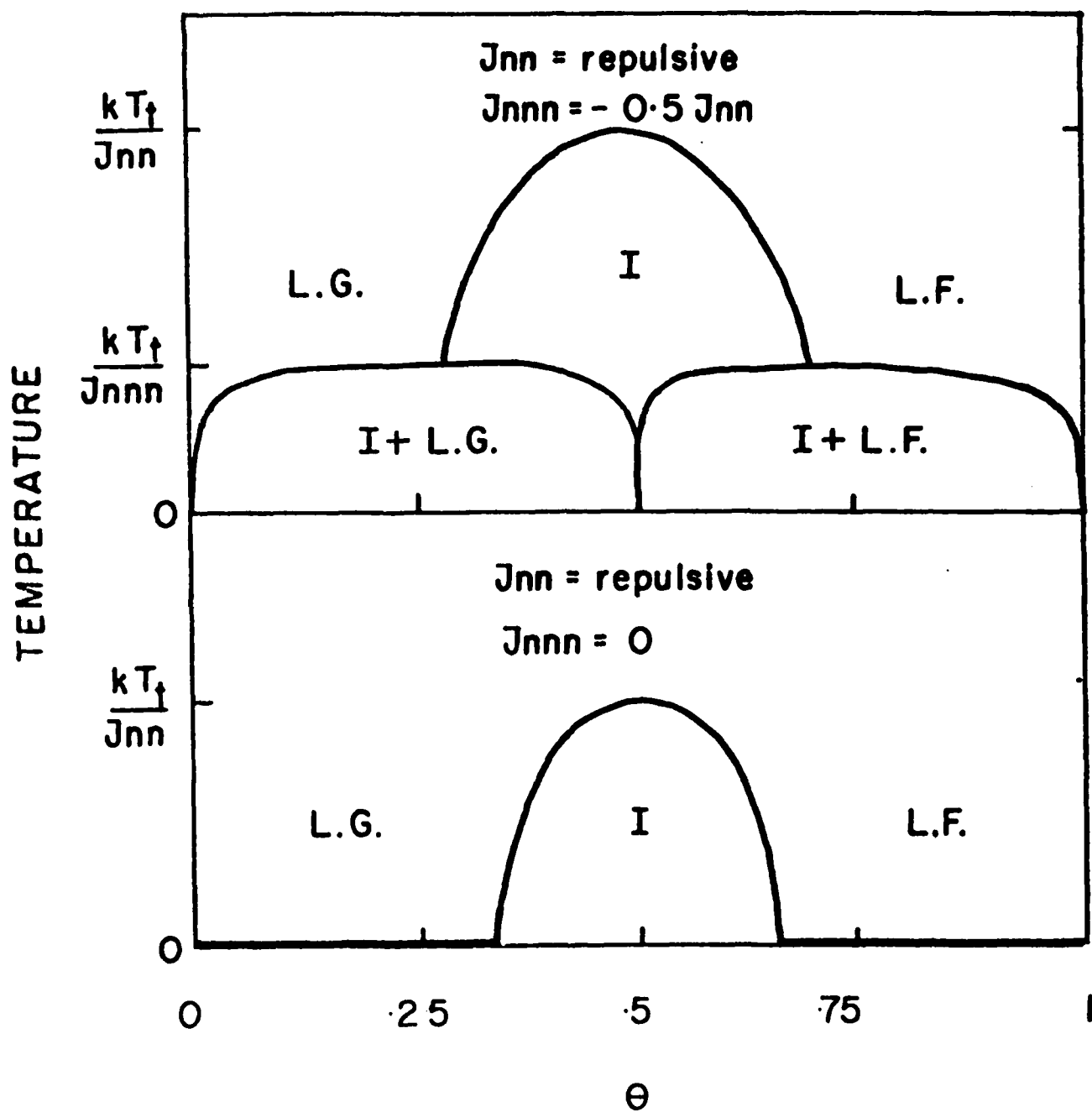
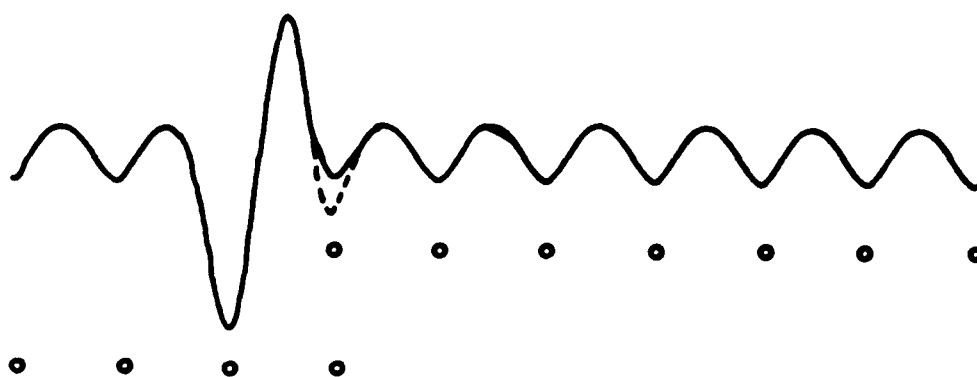
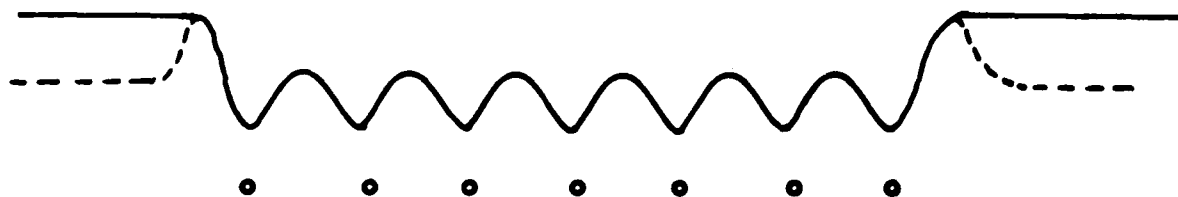


Fig. 4



STEP



MOSAIC

Fig. 5